

FLAME RETARDANTS

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OVERVIEW

Each year, Americans report over three million fires leading to 29,000 injuries and 4,500 deaths (1). The direct property losses exceed \$8 billion (1) and the total annual cost to our society has been estimated at over \$100 billion (2). Personal losses occur mostly in residences where furniture, wall coverings, and clothes are frequently the fuel. Large financial losses occur in commercial structures such as office buildings and warehouses. Fires also occur in airplanes, buses, and trains.

Fires occur when an ignition source, a match, cigarette, or stove burner, meets a flammable product such as a chair, wall, or scattered papers. The heat from the source breaks down polymer strands in the material, creating (generally endothermically) chemical fragments that vaporize. At a sufficiently high temperature, these fragments react with the oxygen in the air to release more heat. Some of this heat radiates or convects back to the product, breaking down more polymeric strands, yielding more gas-phase fuel, etc. Life- and property-threatening fires result when the rate of heat feedback to the product exceeds the sum of the heat dispersed from the combustion environment and the marginal enthalpy required to produce a steady stream of vapor-phase pyrolyzate.

Understanding of fires dates to the nineteenth century. The advent of modern fire fighting techniques and equipment has meant less destruction of cities or whole buildings. Additionally, fire-resistant building design usually contains fires to parts of structures. However, a high fuel load in either a residence or a commercial building can overwhelm even the best of building construction.

Terminology

A number of adjectives have been used to describe a product having an apparently low contribution to a fire. Nonquantitative terms such as fireproof, flameproof, self-extinguishing, nonburning, and noncombustible, have been used and have often led to confusion regarding the relative fire safety of different materials. Additionally, a product is sometimes improperly described by a component material rating under a fire test, a V-0 rating in the UL 94 test, or a building code provision, a 25 flame spread limit for wall coverings using the ASTM E84 method.

These ambiguities eventually led the Federal Trade Commission to take action in the case of cellular plastics and to restrict the use of such terminology (3). This action, in addition to the prohibition placed on the use of certain terminology, requires the use of a caveat whenever the results of burning tests are cited. Much of the older literature, however, as well as some of the more recent publications, use this restricted terminology.

Some pertinent definitions include *fire retardant* (*flame retardant*), used to describe polymers in which basic flammability has been reduced by some modification as measured by one of the accepted test methods; *fire-retardant chemical*, used to denote a compound or mixture of compounds that when added to or incorporated chemically into a polymer serves to slow or hinder the ignition or growth of fire, the foregoing effect occurring primarily in the vapor phase; *materials*, single substances of which things are constructed that may be composed of single or blended polymers, may be layered or fiber-reinforced, and might contain a variety of additives; and *products*, consumer items made of one or more materials.

Measuring Fire Performance of Products

Laws have been promulgated to improve the fire performance of everyday fuels. Most of the fire test methods in regulations have been developed by consensus

standards organizations in response to a particular fire hazard. The two leading entities are the American Society for Testing and Materials (ASTM) and the National Fire Protection Association (NFPA). Methods are then referenced in the model building codes, such as the Standard Building Code (Southern Building Code), Basic Building Code (Building Code Officials Administration International), and the Uniform Building Code (International Conference of Building Officials), as well as NFPA's National Fire Codes, National Electrical Code, and Life Safety Code. Selected portions of these structures are in turn incorporated into laws by a governmental jurisdiction. In addition, there are a number of voluntary practices. For example, Underwriters Laboratories (UL) allows the use of its endorsement on products that meet their test criteria, and the upholstered furniture industry has adopted voluntary cigarette ignition-resistance standards.

Fire test methods attempt to provide correct information on the fire contribution of a product by exposing a small sample to conditions expected in a fire scenario. Methods can be viewed in two ways: the first entails the strategy of the fire test, ignition resistance or low flammability once ignited; the second addresses the test specimen, a sample representative of the product or a sample of a material that might be used in the product. Fire science has progressed markedly since the older test methods were developed and it is known that the basis for many of these tests is doubtful. Results from older tests must be used with great care.

The susceptibility of a product to an ignition source can be measured by flame or heat impingement tests, such as UL 94 (4) or NFPA 260/261 (5), or by ignition delay times in an apparatus such as the Cone Calorimeter (6). In UL 94, a vertical strip of a material is ignited at the bottom and after the burner is removed, one observes whether burning is sustained. This is an example of a material test that results in a simple flammability class assignment. The NFPA cigarette ignition tests are examples of similar tests for a product. There, a cigarette is laid on a reduced-scale mockup of a seat cushion to see whether ignition occurs. The Cone Calorimeter is an apparatus used to measure flammability properties of a product. A cutting representative of the product is exposed to radiant energy typical of a fire of concern. The principal measurement is that of the rate of heat release. Time to ignition can also be determined and used as an indication of ignition susceptibility.

Clearly, fewer ignitions would reduce the number of fires. However, once ignited an ignition-resistant material may burn with a higher intensity than a more easily ignited counterpart (7). Moreover, successful ignition-resistance test performance is not proof of fire prevention. The real world situation may be more severe than the test design, larger ignition sources may occur or thermal radiation from other burning objects could increase the ease of ignition. Thus many elements of fire protection practice presume that ignition can occur. It is then desirable that products burn sufficiently slowly that the fire does not grow rapidly to threatening size, does not ignite adjacent items, and can be readily and simply extinguished. Therefore the controlling characteristic variable is the rate of heat release of the product. Methods have been developed for accurate measurement of rate of heat release (8,6). There is research relating these rates to the performance of products (9,10).

The assessment of the contribution of a product to the fire severity and the resulting hazard to people and property combines appropriate product flamma-

bility data, descriptions of the building and occupants, and computer software that includes the dynamics and chemistry of fires. This type of assessment offers benefits not available from stand-alone test methods: quantitative appraisal of the incremental impact on fire safety of changes in a product; appraisal of the use of a given material in a number of products; and appraisal of the differing impacts of a product in different buildings and occupancies. One method, HAZARD I (11), has been used to determine that several commonly used fire-retardant-polymer systems reduced the overall fire hazard compared to similar nonfire retarded formulations (12).

Methods for Improved Performance

The materials of attention in promoting fire safety are generally organic polymers, both natural, such as wood (qv) and wool (qv), and synthetic, nylon (see POLYAMIDES), vinyl, and rubber (qv). Less fire-prone products generally have either inherently more stable polymeric structures or fire-retardant additives. The former are usually higher priced engineering plastics (qv) which achieve increased stability at elevated temperatures by incorporating stronger (often aromatic) chemical bonds in the backbone of the polymer (13). Examples are the polyimides, polybenzimidazoles, and polyetherketones. There are also some advanced polymers, such as the polyphosphazenes and the polysiloxanes, which have strong inorganic backbones. Thermally stable pendent groups are also necessary. Strongly bonded polymers may, however, be brittle or difficult to process.

Fire-retardant additives are most often used to improve fire performance of low-to-moderate cost commodity polymers. These additives may be physically blended with or chemically bonded to the host polymer. They generally effect either lower ignition susceptibility or, once ignited, lower flammability. Ignition resistance can be improved solely from the thermal behavior of the additive in the condensed phase. Retardants such as hydrated alumina add to the heat capacity of the product, thus increasing the enthalpy needed to bring the polymer to a temperature at which fracture of the chemical bonds occurs. The endothermic volatilization of bound water can be a significant component of the effectiveness of this family of retardants. Other additives, such as the organophosphates, change polymer decomposition chemistry. These materials can induce the formation of a cross-linked, more stable solid and can also lead to the formation of a surface char layer. This layer both insulates the product from further thermal degradation and impedes the flow of potentially flammable decomposition products from the interior of the product to the gas phase where combustion would occur.

Flame retardants function in the vapor phase where the enthalpy-generating combustion reactions occur. Halogen-containing species, for instance, can be selected to vaporize at the same temperature as the polymer fragments. Coexisting in the reactive area of the flame, the halogens are effective at decreasing the concentrations of the free radicals that propagate flames, thus reducing the flame intensity, the enthalpy returned to the product, and the burning rate, in that order. For small ignition sources the use of flame retardants can produce self-

extinguishment. More intense sources may overwhelm the flame retardant, necessitating either a higher concentration or an alternative choice of additive.

Useful materials incorporating fire-retardant additives are not always straightforward to produce. Loadings of 10% are common, and far higher levels of flame retardants are used in some formulations. These concentrations can have a negative effect on the properties and functions for which the materials were originally intended. Product-specific trade-offs are generally necessary between functionality, processibility, fire resistance, and cost.

Nonetheless a large number of fire-retardant additives are possible. The development of the field of fire-retardant additives has its origins in three efforts: the nineteenth century systematic studies of Gay-Lussac, Perkin's discovery that stannates and tungstates helped make treatment with ammonium salts water-resistant, and the discovery in the 1930s of the effect of mixing antimony oxide with organic halogen compounds (14). Research has led to a diversity of additives and a thriving market. Fire retardants are now the most used plastics additives, exceeding 40% of a \$1 billion market in 1991 (15). This market is expected to continue to increase. Table 1 gives the principal groups of chemicals and their relative use. However, there is an ongoing debate over the possible risks of halogenated, especially brominated, fire retardants (15). As can be seen from Table 1, brominated retardants are a significant fraction of the market. Whereas no ban on usage has been issued as of this writing, more data and continued discussions are expected. The issues under debate are (1) the burning of halogenated combustibles produces toxic smoke, and international studies show that most fire victims die from smoke inhalation. The smoke from all fires is noxious. It has been shown that if the fire retardant significantly decreases the burning rate of the product, the reductions in smoke and heat yields are more important to survivability than a modest increase in the toxic potency of the smoke (12); (2) the burning of halogenated combustibles produces corrosive smoke, which results in additional damage to electronic components, etc. The smoke from nonhalogenated polymers is also corrosive and the fire safety community is in the process of developing methods to characterize this property of smoke; (3) the incineration of

Table 1. Flame-Retardant Market Volume^a

Group	1986, t	1991	
		t	\$ × 10 ⁶
phosphate esters	20	18	50
halogenated phosphates	13	16	46
chlorinated hydrocarbons	15	15	31
brominated hydrocarbons	28	36	160
brominated bisphenol A	16	18	37
antimony trioxide	22	25	85
borates	8	8	10
aluminum trihydrate	140	170	85
magnesium hydroxide	2	3	6
<i>Total</i>	<i>264</i>	<i>301</i>	<i>510</i>

^aCourtesy of the TPC Business Research Group.

halogenated combustibles may produce significant amounts of dioxin- and furan-like species. Laboratory combustion experiments need to be compared with measurements of the effluent from properly designed and operated incinerators.

Another factor potentially affecting the market for halogenated fire retardants is the waste disposal of plastics (see WASTES, INDUSTRIAL). As landfill availability declines or becomes less popular, two alternatives are incineration and recycling (qv). The nature of the combustion products from halogenated products requires careful construction and maintenance of incinerators (qv) to avoid damage to the incinerator itself and a public health problem from the exhaust. The ease of recycling used products also has a potential effect on fire retardants.

Flame-retardant additives are capable of significant reduction in the hazard from unwanted fires, and techniques are now available to quantify these improvements. Combined with an understanding of fire-retardant mechanisms, polymer-retardant interactions, and reuse technology, formulations optimized for public benefit and manufacturing practicality can be selected.

BIBLIOGRAPHY

"An Overview" under "Flame Retardants" in *ECT* 3rd ed., Vol. 10, pp. 348-354, by J. W. Lyons, National Bureau of Standards.

1. M. J. Karter, Jr., *NFPA J.* **86**(5), 32 (1992).
2. W. P. Meade, *A First Pass at Computing the Cost of Fire in a Modern Society*, The Herndon Group, Inc., Chapel Hill, N.C., 1991.
3. *Fed. Reg.* **40**(12), 255 (1975).
4. *Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*, UL-94, Underwriters Laboratories, Northbrook, Ill., 1991.
5. "Cigarette Ignition Resistance of Components of Upholstered Furniture," NFPA 260, and "Resistance of Mockup Upholstered Furniture Material Assemblies to Ignition by Smoldering Cigarettes," NFPA 261, in *National Fire Codes*, National Fire Protection Association, Quincy, Mass., 1992.
6. *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter*, ASTM E1354-90a, American Society for Testing and Materials, Philadelphia, Pa., 1991.
7. J. W. Rowen and J. W. Lyons, *J. Cell. Plast.* **14**(1), 25 (1978).
8. *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products*, ASTM E906-83, American Society for Testing and Materials, Philadelphia, Pa., 1991.
9. V. Babrauskas, *SFPE Technology Report 84-10*, Society of Fire Protection Engineers, Boston, Mass., 1984.
10. R. G. Hill, T. I. Eklund, and C. P. Sarkos, *DOT/FAA/CT-85/23*, Federal Aviation Administration Technical Center, Atlantic City, N.J., 1985.
11. R. D. Peacock, W. W. Jones, R. W. Bukowski, and C. L. Forney, *HAZARD I—Fire Hazard Assessment Method*, version 1.1, NIST Handbook 146, National Institute of Standards and Technology, Gaithersburg, Md., 1991.
12. V. Babrauskas and co-workers, *Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products*, NBS Special Publication 749, National Bureau of Standards, Gaithersburg, Md., 1987.

13. R. G. Gann, R. A. Dipert, and M. J. Drews, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, Inc., New York, 1986, pp. 154-210.
14. J. W. Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970, Chapt. 5.
15. S. J. Ainsworth, *Chem. Eng. News*, **70**, 34 (Aug. 31, 1992).

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